

Thermal Stability of Hydrocarbon Radicals

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ABSTRACT

This paper reviews the present state of knowledge regarding the stability of hydrocarbon radicals. We will begin with some definitions regarding thermodynamic and kinetic stability and general comments justifying our interest. A number of the important issues dealing with the accurate determination of these properties will be discussed. This will be followed by a survey of some of the problems and controversies regarding correct values. Finally, thermodynamic and kinetic data bearing on the stability of the radicals will be summarized.

BACKGROUND

The reactions of hydrocarbons in the gas phase and non-polar media frequently proceed through free radical mechanisms. Quantitative understanding of the temporal behavior of such processes depends on knowledge of the thermodynamic and kinetic properties of the radicals. The thermodynamic stability of any compound can most conveniently be expressed in a quantitative sense in terms of its free energy or equilibrium constant of formation. This can be expressed as,

$$\Delta F = \Delta H - T\Delta S = -RT \ln K_p \quad [1]$$

$$K_p = k_f/k_r(RT)^n \quad [2]$$

where the reference state is for the elements at 1 bar and 298 K, k_f and k_r are the rate constants in the two directions and n represent the order of the reaction. Thermodynamic properties serve as limits for kinetics and the basis for the estimation and evaluation of kinetic information. A particularly important application is its use for the calculation of the rate constant in one direction if that for the reverse reaction is known. Alternatively, when the rates in both directions have been measured, the reproduction of the equilibrium property serves as an important check of the validity of the data. Thermodynamic properties of radicals are not only important for their own sake but can be used to infer the chemical stability and reactivity of the compounds formed by any two radicals. This is largely due to the fact that radical combination rate constants do not vary greatly.

Enthalpy and entropy define the properties of a molecule in terms of energetics and structure (1). Traditionally, they form the basis for estimation (2). Modern day computational packages (3) permit their direct calculation from ab initio quantum mechanics. Such methods work quite well for small radicals and are in general more reliable with respect to structural or entropic factors than the energies. In time, these methods will play an ever more important role in defining the properties of radicals. In the meantime dependence must remain with experimental determinations. A key role for accurate measurements is as a means of validating calculations. A combination of group additivity and small molecule calculational results should in principal give all the information necessary for the determination of the thermodynamic properties of larger entities.

As suggested above, the thermodynamic properties of radicals can be determined through the measurement of the equilibrium constant (1). From measurements at one temperature enthalpies can be determined if entropies can be estimated. This is usually known as the 3rd law method. Alternatively, from determinations of the equilibrium constant as a function of temperature, the enthalpy of the process can be determined from the slope or

$$d[\ln K_p]/d(1/T) = -\Delta H/R. \quad [3]$$

This is known as the second law method. Substituting back into Eq 1 then leads to a determination of the entropy. In order to determine the property of a radical the thermodynamic properties of the other compounds for the reaction must be known and if reactions are carried out at temperatures different than 298 K heat capacity corrections must be made.

Much effort has been devoted to determining the enthalpies of free radicals (4,5). They are directly related to the bond dissociation energies of the molecular entity from which the radicals are formed and is a convenient marker for molecular stability or reactivity. Many measurement methods lead only to the determination of the energies. If one applies the second

law method, then a slope can be determined without the need for an absolute value of the equilibrium constant, if the calibration factor does not vary over the temperature range used and assumptions can be made about the reverse process. Complete quantitative description in the context of molecular stability will also require knowledge of the entropy. Our knowledge and understanding of radical structure and vibrational frequencies are such that for the less complex radicals, measurements exist or they can be estimated with considerable accuracy. There remains uncertainties for larger species. This is particularly the case for the molecular motions associated with low frequency vibrations. Unfortunately, these are also the largest contributors to the entropies. In the case of simple hydrocarbon radicals, the important issues are the frequency of the umbrella motion at the radical site. It is in fact uncertain as to whether they can be represented in the simple harmonic oscillator approximation. Another issue is the barrier to internal rotation of rotors at the radical site.

Kinetic stability(6) can most readily be defined in terms of the rate expressions for decomposition of radicals or the parent hydrocarbon,

$$k = A_{\infty} T^n \exp(-E_{\infty}/RT) s^{-1} \quad [4]$$

where we have chosen to write the rate expression in the modified Arrhenius form. Over short ranges, data can be written in the regular Arrhenius form where $n=0$. The infinities are given to define the results in terms of the rate constant in the limiting high pressure region. This means the results are for a system where the distribution function for the molecule is Boltzmann. High pressure rate expression for decomposition is a fundamental property of a molecule and is given in this form in order to differentiate it from the more general case where the distribution function are perturbed when the chemical lifetimes become shorter than energy transfer times, leading to a distorting of the Boltzmann distribution. The high pressure rate expressions are one of the fundamental inputs for the understanding of many complex reaction systems. They define the non-reactive lifetimes of the radicals and play a key role in the evolution of such systems. Even for the cases where energy transfer is important, the high pressure rate expression is the basis upon which estimates for energy transfer effects are made. As suggested earlier, these rate expressions can be used to derive or be derived from the thermodynamics.

EXPERIMENTAL METHODS

All experimental procedures for determining the thermodynamic and kinetic stability of radicals involve quantitative measurement of some property associated with their generation or destruction. Kinetic measurements in both directions is a prime method for determining equilibrium constants of formation. The reliable values that are now available owe much to the understanding of how to carry out accurate kinetic measurements. The first prerequisite is to find systems that are mechanistically unambiguous. This requirement is aided by the sensitivity of modern detection methods. It is thus possible to work under conditions where there are no ambiguity regarding the process being studied. Table 1 summarizes a variety of kinetic methods that have made significant contributions to the determination of the thermodynamic properties of hydrocarbon radicals. In general, the thermal decomposition reactions are carried out at the highest temperatures, the radical decompositions at intermediate temperatures while the metathesis and ion-molecule reactions are at the lowest or ambient temperatures. The choice of a technique is highly dependent on the availability of a suitable precursor. This is particularly true at the lower temperatures. At the higher temperatures more channels are opened up. However this can lead to mechanistic complications.

An alternative approach is to subject a molecule to some form of physical excitation such as a photon or electron which leads to the formation of the radical in question and then observing their formation and deducing the energetics on the basis of an energy balance. Since molecules have a distribution of energies an important issue has always been the proper selection of reaction thresholds. As with the kinetic methods, the availability of an appropriate precursor is an important determinant of what can be measured. Since this is a physical method, the most reliable numbers are for the smaller species. Furthermore, as with kinetic methods, earlier workers were much too optimistic regarding measurement accuracy. The tendency has been to reproduce the kinetic results that are now known to be in error. Here again improvements in understanding and techniques are leading to more accurate determinations.

RESULTS

A: Thermodynamic Stability: Table 2 contains a summary of data on bond dissociation energies that can be derived from heats of formation data. These have largely been derived from the methods summarized in Table 1. Also included in Table 2 are the recommendations of

Table 1: Kinetic procedures and methods used in determining the thermodynamic properties of organic radicals.(8,9)

Process	Method	Reaction Type (example)
Thermal Decomposition	Single Pulse Shock Tube Flow and Static systems. Detection of stable products	$R_1-R_2 \rightleftharpoons R_1+R_2$ $((tC_4H_9)_2 \rightleftharpoons 2 tC_4H_9)$
Radical Combination	Photolytic generation of Radicals and spectroscopic Detection	
Radical Decomposition	Photolytic and thermal generation of radicals. Detection of stable products or decay of radicals	$R \rightleftharpoons H/CH_3 + \text{olefin}$ $nC_3H_7 \rightleftharpoons C_2H_4 + CH_3$
Radical Addition	Decay of photolytically generated small radicals	
Metathesis of halogenated organics	Photolytic generation of radicals Followed by their decay	$X + RH \rightleftharpoons R + HX$ $Br + tC_4H_9$
Ion-molecule equilibria	Metathesis reaction involving ions in flow system. Mass spectrometric detection of reactants and products	$C_3H_6 + CH_3O \rightleftharpoons$ $C_3H_5 + CH_3OH$

McMillen and Golden(4) published in 1982 which are based largely on iodination results. It can be seen that in all cases except for methyl, for which the best results are from physical approaches, there have been significant increases in the heats of formation. This is surprising to those who are not intimately acquainted with the field. Since much of chemistry is involved in the breaking or forming of bonds, there is a natural attempt to interpret experimental observations in terms of bond dissociation energies. Unfortunately, it is now clear that earlier investigators were much too optimistic regarding the accuracy of their estimates.

The following contains a brief historical sketch of the sequence of studies of which the data in Table 2 represent hopefully the final correct values. The first systematic investigation of the thermodynamic properties of hydrocarbon radicals were the studies of Butler et al (9) where the kinetics of the decomposition of the alkyl iodides was interpreted in terms of the breaking of the carbon-iodine bond. Subsequent analysis revealed that the decomposition reaction is in fact a radical chain process with the additional possibility of a molecular decomposition channel. A few years latter, Szwarc and coworkers (10) studied inhibited decomposition of simple hydrocarbons in flow systems. Radical processes were suppressed by the addition of the radical inhibitor, toluene. It is now clear that the conditions in the flow reactor were very poorly defined. The consequence was that the rate expressions are all now known to be characterized by low A-factors and activation energies. Several years latter Benson and coworkers(1) used iodination kinetics to determine bond energies. The specific reactions used in their work were largely those involving the bimolecular attack of iodine atom on alkyl iodide to form the hydrocarbon radical and the iodine molecule or the reverse. A number of major errors were corrected leading once again to large increases in the measured heats of formation.

These results which first appeared in the early 1960s were summarized in a 1982 article in Annual Reviews of Physical Chemistry (4) and for many years represented the generally accepted values. However beginning with the single pulse shock tube work in the late 1960s(11) it became increasingly difficult to fit experimental results with such heats of formation. Some of the consequences are summarized in Table 2 and represent a further increase of 10-20 kJ/mol. The correctness of these numbers is attested by the large volume of experimental data that can now reproduce the thermodynamic properties of the radicals. Indeed, if errors are substantially larger than the estimated uncertainties, this will call into question much that is believed to be understood about experimental gas phase kinetics. Actually, of all the numbers given in Table 2, only that for t-butyl radical is still subject to any controversy. It should also be noted that there may also uncertainties of the order of several kJ/mol in the heats of formation of the larger alkanes (12). This will of course be directly reflected in the errors of the radicals.

The ultimate importance of data such as summarized in Table 2 is as a basis for estimation. It is of interest to consider the consequences of errors in such values. If they are directly reflected in the rate or equilibrium constants, then an error of 5.5 kJ/mol will lead to an

Table 2: Heats of formation for some hydrocarbon radicals and their corresponding bond dissociation energies. (7,8) Heats of formation in italics are from McMillen and Golden (4)

R1/R2 (kJ/mol)	(Ref 4)	H	CH ₃ 147 ± 1	C ₂ H ₅ 119 ± 2	i-C ₃ H ₇ 90 ± 2	t-C ₄ H ₉ 48 ± 3
CH ₃ (147 ± 1)	(147±1)	440	378	370	370	360
C ₂ H ₅ (119 ± 2)	(108±4)	422	370	364	362	352
n-C ₃ H ₇ (100 ± 2)	(88±4)	422	373	365	362	353
i-C ₃ H ₇ (90 ± 2)	(76±4)	412	372	364	361	343
s-C ₄ H ₉ (69 ± 2)	(54±8)	413	370	362	356	336
i-C ₄ H ₉ (70 ± 2)		422	371	363	360	341
t-C ₄ H ₉ (48 ± 3)	(39±4)	400	360	352	341	321
t-C ₅ H ₁₁ (28 ± 3)		402	361	354	334	314
C ₃ H ₅ (allyl) (171 ± 3)	(164±6)	368	318	311	309	302
C ₃ H ₅ (propenyl) (267 ± 3)		465	421	414		
C ₄ H ₇ (isobutenyl) (138 ± 3)		373				
C ₄ H ₇ (methylallyl) (158 ± 3)		375				
C ₃ H ₃ (propargyl) (351 ± 2)		384	333	326	322	
C ₄ H ₅ (methylpropargyl) (313 ± 2)		385				
C ₆ H ₅ (phenyl) (341 ± 4)		475	436	428	423	408
C ₆ H ₅ CH ₂ (benzyl) (207 ± 4)	(200± 6)	375	324	318	317	309

error of a factor of 10 in these quantities at room temperature and a factor of 2 at 1000 K. Correspondingly an error of 21 kJ/mol will lead to an error of 4 orders of magnitude at room temperature and a factor of 10 at 1000 K. This is a direct reflection of the logarithmic dependence of the rate and equilibrium constants on the thermodynamic functions. It is clear that the accuracy that are now attainable is probably sufficient for higher temperature applications but is still somewhat unsatisfactory for room temperature use.

B: Kinetic Stability: The kinetic stability of hydrocarbon molecules and radicals that are consistent with the thermodynamics are summarized in Tables 3-4. Table 3 contains experimental data on the decomposition of a number of simple alkanes and alkynes and are the results of single pulse shock tube studies. They have been a major factor in the development of the results given in Table 2. Some noteworthy factors are the following: (a) It can be seen that at the high temperature end of the experimental studies, for a particular type of reaction the A-factors do not vary greatly except for the influence of reaction path degeneracy and differences in rate constants are largely due to activation energy changes. (b) It is possible to discern a difference in the A-factors for the cases where alkyl radicals are formed as opposed to the formation of a resonance stabilized radical. This difference is explicable in terms of the stiffer structure of the latter. (c) Over the entire temperature range, for the bond breaking reaction of alkanes there is a negative curvature of the Arrhenius plot. This is much larger for the most highly substituted hydrocarbon. Actually, the lowest temperature results are derived from the conversion of the combination rate constants to the dissociation values through the equilibrium

Table 3: Summary of rate expressions for the decomposition of some alkanes and alkynes

Reaction	Rate Expressions
Alkanes 1000-1200K	
$k(iC_3H_7-tC_4H_9 \Rightarrow iC_3H_7 + tC_4H_9)$	$2.5 \times 10^{16} \exp(-36800/T) s^{-1}$
$k(iCH_3-tC_4H_9 \Rightarrow CH_3 + tC_4H_9)$	$1 \times 10^{17} \exp(-41100/T) s^{-1}$
$k(C_2H_5tC_5H_{11} \Rightarrow C_2H_5 + tC_5H_{11})$	$6 \times 10^{16} \exp(-38800/T) s^{-1}$
$k(iC_3H_7-tC_5H_{11} \Rightarrow iC_3H_7 + tC_5H_{11})$	$2.3 \times 10^{16} \exp(-35900/T) s^{-1}$
$k(sC_4H_9-tC_4H_9 \Rightarrow sC_4H_9 + tC_4H_9)$	$3 \times 10^{16} \exp(-36400/T) s^{-1}$
$k(sC_4H_9-sC_4H_9 \Rightarrow sC_4H_9 + sC_4H_9)$	$3.5 \times 10^{16} \exp(-37900/T) s^{-1}$
$k(cC_6H_{11}-tC_4H_9 \Rightarrow cC_6H_{11} + tC_4H_9)$	$3 \times 10^{16} \exp(-37400/T) s^{-1}$
$k(tC_4H_9-tC_4H_9 \Rightarrow tC_4H_9 + tC_4H_9)$	$3 \times 10^{16} \exp(-34500/T) s^{-1}$
Alkynes 1000-1200 K	
$k(HCCCH_2-nC_3H_7 \Rightarrow HCCCH_2 + nC_3H_7)$	$8 \times 10^{15} \exp(-36300/T) s^{-1}$
$k(HCCCH_2-iC_4H_9 \Rightarrow HCCCH_2 + iC_4H_9)$	$1.2 \times 10^{16} \exp(-36700/T) s^{-1}$
$k(CH_3CCCH_2-nC_3H_7 \Rightarrow CH_3CCCH_2 + nC_3H_7)$	$1.5 \times 10^{16} \exp(-36800/T) s^{-1}$
$k(HCCCH_2-sC_4H_9 \Rightarrow HCCCH_2 + sC_4H_9)$	$8 \times 10^{15} \exp(-35000/T) s^{-1}$
$k(HCCCH_2-iC_3H_7 \Rightarrow HCCCH_2 + iC_3H_7)$	$5 \times 10^{15} \exp(-34800/T) s^{-1}$
Alkanes 300 - 1200 K	
$k(C_2H_5-C_2H_5 \Rightarrow 2 C_2H_5)$	$4.4 \times 10^{25} (1/T)^{2.7} \exp(-44441/T) s^{-1}$
$k(iC_3H_7-iC_3H_7 \Rightarrow 2 iC_3H_7)$	$1.6 \times 10^{31} (1/T)^{4.2} \exp(-43897/T) s^{-1}$
$k(tC_4H_9-tC_4H_9 \Rightarrow 2 tC_4H_9)$	$5.5 \times 10^{38} (1/T)^{6.45} \exp(-41065/T) s^{-1}$

Table 4: Derived rate expressions for radical decomposition, based on thermodynamics and rate constant for addition 300–900 K

Reaction	Rate Expressions s ⁻¹	Rate Constants at 750 K s ⁻¹
nC ₃ H ₇ = C ₂ H ₄ + CH ₃	1.2x10 ¹³ exp(-15260/T)	1.8x10 ³
sC ₄ H ₉ = C ₃ H ₆ + CH ₃	9x10 ¹² exp(-14770/T)	2.5x10 ⁴
iC ₃ H ₇ = C ₃ H ₆ + H	2.6x10 ¹³ exp(-18730/T)	3.7x10 ²
sC ₄ H ₉ = 1-C ₄ H ₈ + H	1.3x10 ¹³ exp(-18320/T)	3.2x10 ²
sC ₄ H ₉ = c-C ₄ H ₈ + H	4.2x10 ¹² exp(-17500/T)	3.1x10 ²
sC ₄ H ₉ = t-C ₄ H ₈ + H	4.7x10 ¹² exp(-17100/T)	5.8 x10 ²
tC ₄ H ₉ = C ₄ H ₈ + H	8.5x10 ¹³ exp(-18900/T)	9.7 x10 ²

constant. Rate constants are in fact so small that they are not measurable and thus physically meaningful. The relative invariance of the A-factor at the higher temperatures is in contrast to the situation at the lower temperatures. The consequence is that with the existing data base on thermodynamics and decomposition kinetics it should be fairly straightforward to predict rate constants for decomposition of simple hydrocarbons.

Table 4 contains rate expressions for the decomposition of a number of alkyl radicals(12). The experimental data set of rate expressions for the decomposition of the larger alkyl radicals are unsatisfactory. Even for the same system rate expressions can be widely divergent. The situation is much better regarding rate constants. For such studies radicals must be generated in situ. Furthermore it is likely that many of the studies are in the region where energy transfer effects make significant contributions. However at somewhat lower temperatures there exist very good data on radical addition to olefins or the reverse of the decomposition reaction. Combination of this data with the equilibrium constants leads to rate expressions for decomposition. A check is offered through a match of the rate constants for decomposition at the experimental decomposition temperature. The results on H-bond cleavage is indicative of the effect of methyl substitution. Reaction pathway degeneracy must also be considered. We have also found that the effect of methyl substitution on C-C bond cleavage is very similar to that for the stable compounds (13).

CONCLUSION

Experimental studies have now led to highly accurate values for the thermodynamic and kinetic stability of a large number of hydrocarbon radicals. The techniques that have been employed are extensible to other systems. There is the need for such measurements for many of the larger highly unsaturated radicals with or without resonance stabilization. The increased accuracy requirements under ambient conditions mean that there is still a need to reduce uncertainty limits in all cases. In combination with rapidly developing theory, the expectation is for increasingly accurate predictions of the properties of reactive hydrocarbon systems.

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